Near-IR Phosphorescence of Iridium(III) Corroles at Ambient Temperature

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Materials and Methods

All reagents were purchased from Sigma-Aldrich and were used as received without further purification. All solvents were purchased through the VWR stockroom at Caltech.

Solution state UV-vis absorption spectra were measured using a Cary 50 scanning spectrophotometer with a pulsed xenon lamp as the excitation source. The error in reported wavelength values is at most 0.5 nm. Extinction coefficients were measured for gravimetrically prepared solutions of iridium corroles in toluene, and should be accurate to ±10%.

Steady-state and time-resolved emission measurements were conducted at the Beckman Institute Laser Resource Center. Emission spectra were recorded on samples dissolved in solution (room temperature) or frozen glass (77 K). Samples were degassed by three freeze-pump-thaw cycles. For steady-state emission spectra, the 496.5 nm line of an argon ion laser (Coherent Inova 70) was used to excite samples. Right angle emission was collected via with a Melles Griot Fiber Optic Spectrometer (MGSPEC-2048-SPU). Quantum yields were obtained by comparing signal intensity (corrected through use of a pre-made software file) to a tetraphenylporphyrin standard. Absorption values for the samples at 496.5 nm were recorded on a Hewlett-Packard 8451A diode array spectrophotometer.

For time-resolved measurements, samples were excited at 440 nm. Pulses of 8 ns duration from the third harmonic of a Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series) operating at 10 Hz were used to pump an optical parametric oscillator (OPO, Spectra-Physics Quanta-Ray MOPO-700) to provide laser pulses at 440 nm. Emitted light was detected with a photomultiplier tube (PMT, Hamamatsu R928). PMT current was amplified and recorded using a transient digitizer (Tektronix DSA 602).

Excitation spectra were recorded on a Jobin Yvon Spex Fluorolog-3-11. Sample excitation was achieved via a xenon arc lamp with a monochromator providing wavelength selection. The excitation wavelength was scanned between 300 nm and 700 nm and recorded at 790 nm and 890 nm. Slits of 2 and 10 nm bandpass were used for excitation and emission, respectively. Right angle light emission was sorted using a monochromator and fed into a Hamamatsu R928P photomultiplier tube with photon counting. Short and long pass filters were used where appropriate.

Resonance Raman spectra were recorded using the 488 nm line of an argon ion laser (Coherent Inova 70). Scattered light was sorted by a 0.75 m spectrograph (Spex 750M) and detected with a liquid-nitrogen-cooled CCD (Princeton Instruments).

Synthesis

The syntheses of compounds **1-Ir(tma)$_2$** and **1b-Ir(tma)$_2$** have been reported in a JACS communication [Palmer, J. H.; Day, M. W.; Wilson, A. D.; Henling, L. M.; Gross, Z.; Gray, H. B. *J. Am. Chem. Soc.* **2008,** *130(25),* 7786-7787.], and the synthesis of **1-Ir(py)$_2$** has been reported in a paper in Inorganic Chemistry [Palmer, J. H.; Mahammed, A.; Lancaster, K. M.; Gross, Z.; Gray, H. B. *Inorg. Chem.* **2009.** *48(19),* 9308-9315.]. Syntheses are detailed below for convenience.

5,10,15-*tris*(pentafluorophenyl)corrolatoiridium(III) *bis*(trimethylamine), 1-Ir(tma)$_2$. H_3tpfc (80 mg), $[Ir(cod)Cl]_2$ (335 mg), and K_2CO_3 (140 mg) were dissolved/suspended in 150 mL of degassed THF, and the mixture was refluxed under argon for 90 min (until the corrole fluorescence was negligible to the eye upon long-wave irradiation with a hand-held lamp). Tma N-oxide (110 mg) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the black solution (silica, 4:1 hexanes:CH_2Cl_2) provided purple crystals of **1-Ir(tma)$_2$** (30 mg, 27% yield). ^{1}H NMR (CD_2Cl_2): δ 8.93 (d, 2H), 8.54 (d, 2H), 8.42 (d, 2H), 8.12 (d, 2H), -2.96 (s, 18H). ^{19}F NMR (CD_2Cl_2): δ -139.1 (m, 6H), -156.2 (m, 3H), -164.3 (m, 6H). MS (ESI): 1105.1 ([M^+]), 1046.0 ([M^+-tma]), 986.5 ([M^+-2tma]). UV-vis (toluene, nm, ε in $M^{-1}cm^{-1}$ x 10^{-3}): 390 (51.9), 413 (64.3), 574 (15.9), 640 (5.64).

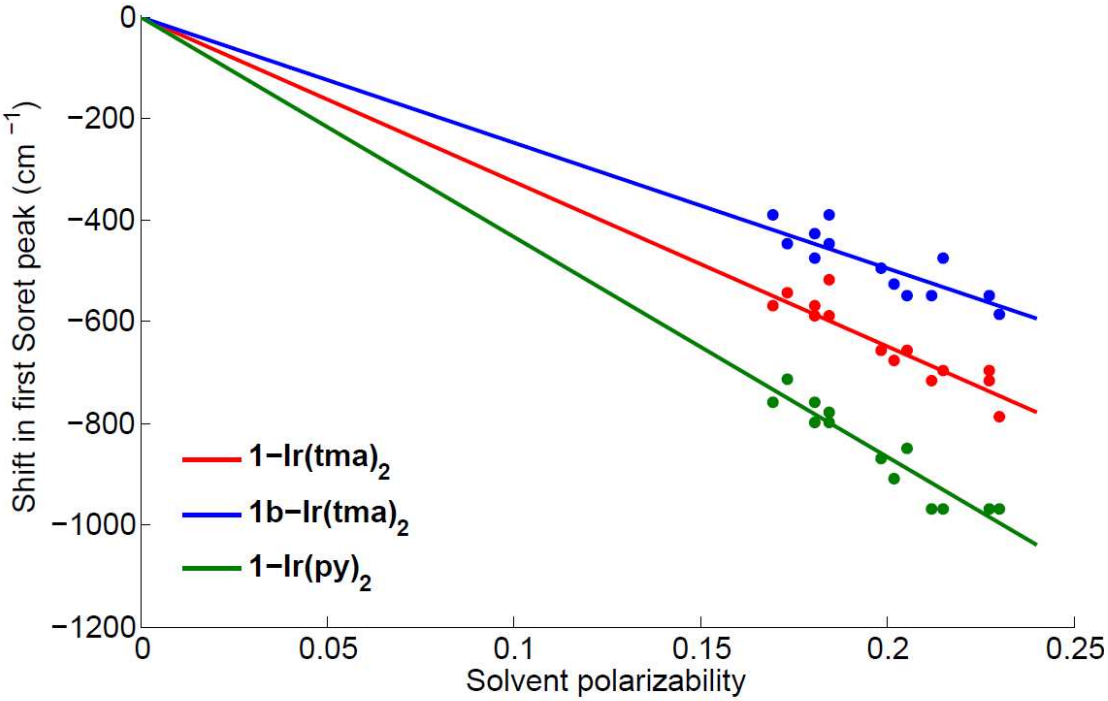
2,3,7,8,12,13,17,18-octabromo-5,10,15-*tris*(pentafluorophenyl)corrolatoiridium(III) *bis*(trimethylamine), 1b-Ir(tma)$_2$. Complex **1-Ir(tma)$_2$** (15 mg) and Br_2 (70 μL) were dissolved in 20 mL MeOH and stirred overnight. Column chromatography (silica, 4:1 hexanes:CH_2Cl_2) of the red solution provided green crystals of **1b-Ir(tma)$_2$** (15 mg, 63% yield). ^{1}H NMR (CD_2Cl_2): δ -2.59 (s, 18H). ^{19}F NMR

(CD_2Cl_2): δ -138.4 (q, 2H), -139.0 (q, 4H), -153.9 (t, 3H), -164.4 (m, 4H), -164.7 (m, 2H). UV-vis (toluene, nm, ε in $M^{-1}cm^{-1}$ x 10^{-3}): 404 (54.0), 424 (62.8), 582 (13.9), 656 (6.15).

5,10,15-*tris*(pentafluorophenylcorrolato)iridium(III) *bis*-pyridine, 1-Ir(py)$_2$. H_3tpfc (40 mg), $[Ir(cod)Cl]_2$ (170 mg), and K_2CO_3 (70 mg) were dissolved/suspended in 75 mL of degassed THF, and the mixture was heated at reflux under argon for 90 min. Pyridine (1 mL) was added, and the solution was allowed to slowly cool to room temperature while open to the laboratory atmosphere. Column chromatography of the forest green mixture (silica, 4:1 hexanes:CH_2Cl_2 followed by 3:2 hexanes:CH_2Cl_2) provided a bright green solution, from which thin, green crystals of **1-Ir(py)$_2$** (26 mg, 50% yield) could be grown by addition of methanol followed by slow evaporation. ^{1}H NMR ($CDCl_3$): δ 8.84 (d, 2H, J = 4.5), 8.53 (d, 2H, J = 4.8), 8.32 (d, 2H, J = 4.8), 8.17 (d, 2H, J = 4.5), 6.21 (t, 2H, J = 7.8), 5.19 (t, 4H, J = 7.0), 1.72 (d, 4H, J = 5.1). ^{19}F NMR ($CDCl_3$): δ -138.68 (m, 6F), -154.84 (t, 2F, J = 22.2), -155.20 (t, 1F, J = 22.2), -163.28 (m, 4F), -163.65 (m, 2F). MS (ESI): 1144.1 ([M^+]). UV-vis (toluene, nm, ε x 10^{-3} $M^{-1}cm^{-1}$): 392 (46.1), 412 (68.3), 584 (19.4), 621 (10.6).

Plotting of Solvatochromic Effects

The refraction of the sodium D line at 20°C in a given solvent was taken to represent its refractive index, n_D^{20}, or simply n. The polarizability of a solvent [f(n)] is related to its refractive index *via* the following relationship: $f(n) = (n^2 - 1)/(2n^2+1)$ [Lakowicz, Joseph R. *Principles of Fluorescence Spectroscopy, 2nd Ed.* **1999,** pg. 189]. The extent of the solvatochromic effect exhibited by an absorbing species in a given solvent is then determined by the slope of the line $E_f = E_v - (solv)[f(n)]$, where E_f is the absorption energy in the solvent, E_v is the absorption energy in vacuum, and (solv) is a factor related to the magnitude of the change in the dipole moment of the chromophore upon excitation. In this formalism, the y-intercept of the line is equal to the theoretical gas-phase absorption energy of the transition under examination. We have made our solvatochromism plots by setting this value equal to zero and plotting the extent of red-shifting in a variety of solvents. This allows for facile comparison of the three corroles, such that the steepness of the slope scales with the magnitude of the separation between the ground and excited state dipole moments. In all cases, the excited state is more polar than the ground state.



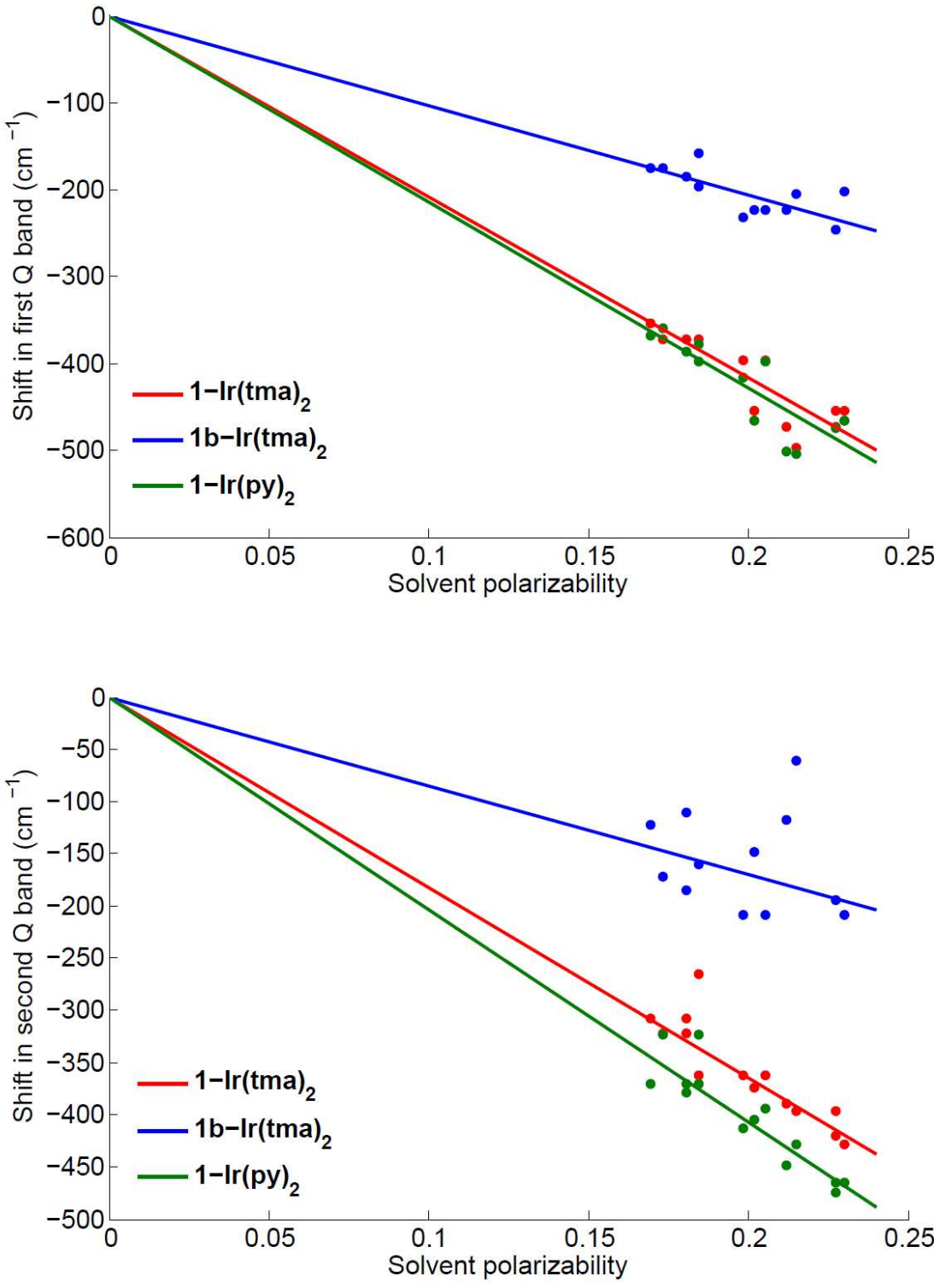


Figure S1. Spectral shifts of the absorption maxima as a function of solvent polarizability for the weaker Soret and both Q absorption bands in various solvents.

Table S1. Slopes and fitting values for solvatochromic effects on each absorption band in the iridium(III) corroles. The correlation values for the Q bands of **1b-Ir(tma)$_2$** are probably poor due to the low intensities of those bands at the concentrations examined.

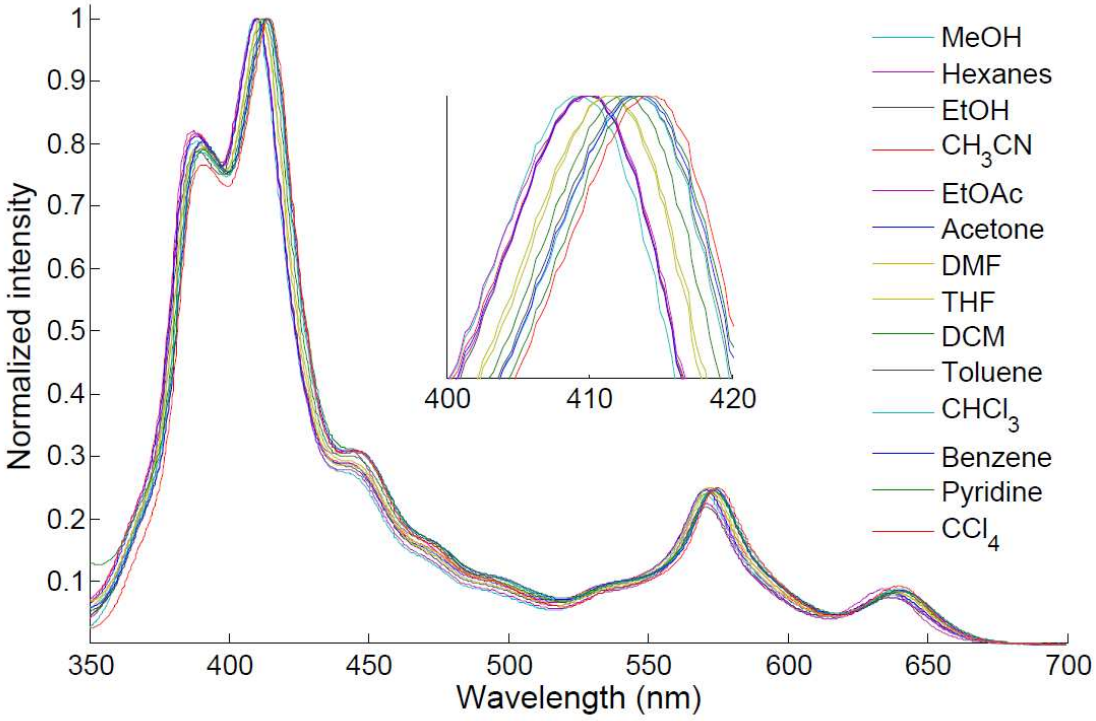
Compound	Band	Slope of shift (f/cm^{-1})	Correlation R^2
1-Ir(tma)2	First Soret	-3200	0.90
	Second Soret	-4600	0.90
	First Q band	-2100	0.77
	Second Q band	-1800	0.91
1b-Ir(tma)2	First Soret	-2500	0.78
	Second Soret	-2900	0.95
	First Q band	-1000	0.60
	Second Q band	-850	0.25
1-Ir(py)2	First Soret	-4300	0.90
	Second Soret	-5000	0.94
	First Q band	-2100	0.75
	Second Q band	-2000	0.89

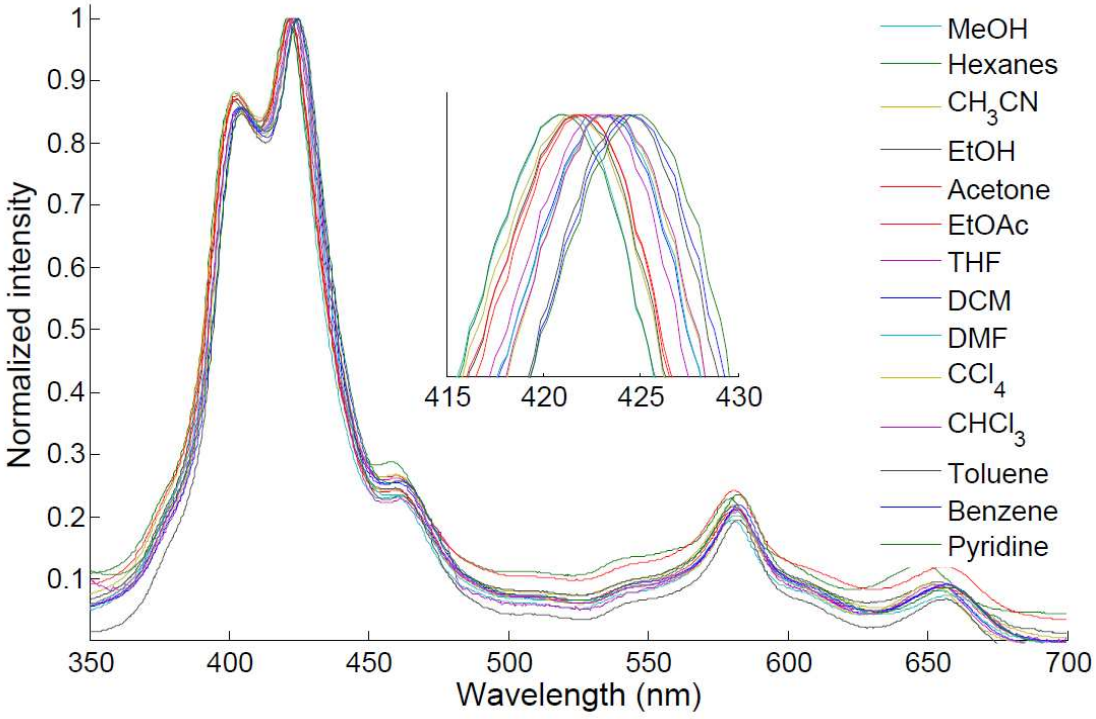
Table S2. Luminescence lifetimes of Ir(III) corroles in methanol at 298 K. This is to illustrate that a non-polar solvent such as toluene is not required by any means to achieve luminescence in our systems. The fact that the corroles are luminescent in MeOH suggests that water-soluble derivatives should luminesce in aqueous solutions.

Compound	τ_{Ar}(μs) [77 K]
1-Ir(tma)$_2$	0.103 [2.82]
1b-Ir(tma)$_2$	0.668 [3.95]
1-Ir(py)$_2$	0.470 [7.57]

Table S1. Refractive indices (nD^{20}), solvent polarizabilities [f(n)], and Ir(III) corrole absorbance maxima (in cm^{-1}) of the solvents used in our solvatochromic experiments (py = **1-Ir(py)$_2$**, br = **1b-Ir(tma)$_2$**, tm = **1-Ir(tma)$_2$**; S1 and S2 = blue and red Soret bands, respectively; Q1 and Q2 = blue and red Q bands, respectively).

Solvent	n_D^{20}	f(n)	pyS1	pyS2	pyQ1	pyQ2	brS1	brS2	brQ1	brQ2	tmS1	tmS2	tmQ1	tmQ2
MeOH	1.33	0.169	25674	24528	17244	16202	24894	23747	17235	15305	25760	24438	17535	15723
CH3CN	1.34	0.173	25720	24528	17253	16250	24839	23702	17235	15256	25786	24390	17516	15708
Acetone	1.36	0.181	25674	24492	17227	16202	24808	23685	17227	15242	25760	24390	17516	15708
Ethanol	1.36	0.181	25634	24474	17227	16194	24857	23702	17227	15316	25740	24390	17516	15723
Hexanes	1.37	0.184	25654	24528	17215	16250	24894	23764	17253	15434	25813	24450	17516	15765
THF	1.41	0.199	25562	24390	17197	16160	24789	23652	17179	15218	25674	24301	17492	15669
DCM	1.42	0.202	25523	24355	17147	16168	24759	23635	17188	15279	25654	24254	17434	15657
DMF	1.43	0.205	25582	24390	17215	16179	24734	23618	17188	15218	25674	24301	17492	15669
CHCl3	1.45	0.212	25465	24301	17112	16124	24734	23635	17188	15309	25615	24201	17416	15642
CCl4	1.46	0.215	25465	24278	17109	16145	24808	23618	17206	15366	25634	24143	17391	15635
Benzene	1.5	0.227	25465	24254	17138	16098	24734	23557	17164	15232	25615	24184	17416	15610
Toluene	1.5	0.227	25465	24278	17138	16108	24734	23557	17164	15232	25634	24201	17434	15635
Pyridine	1.51	0.23	25465	24254	17147	16108	24697	23540	17209	15218	25543	24160	17434	15603


Normalized intensity
Wavelength (nm)
MeOH
Hexanes
EtOH
CH3CN
EtOAc
Acetone
DMF
THF
DCM
Toluene
CHCl3
Benzene
Pyridine
CCl4


Normalized intensity
Wavelength (nm)
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Hexanes
CH3CN
EtOH
Acetone
EtOAc
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Pyridine

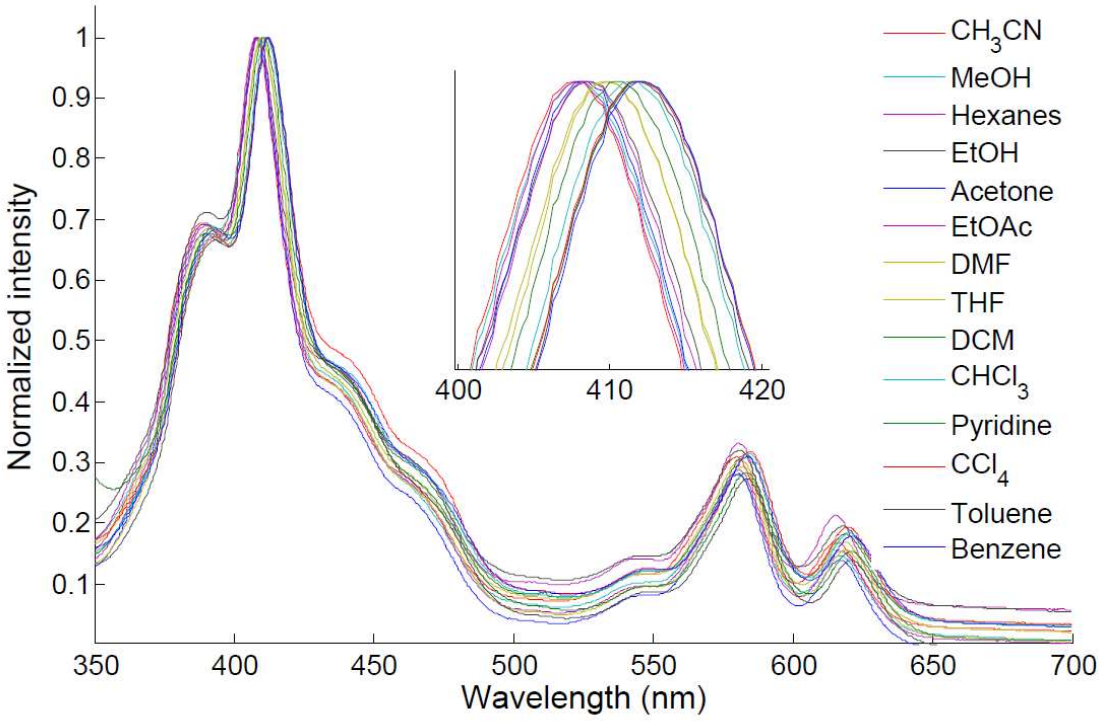
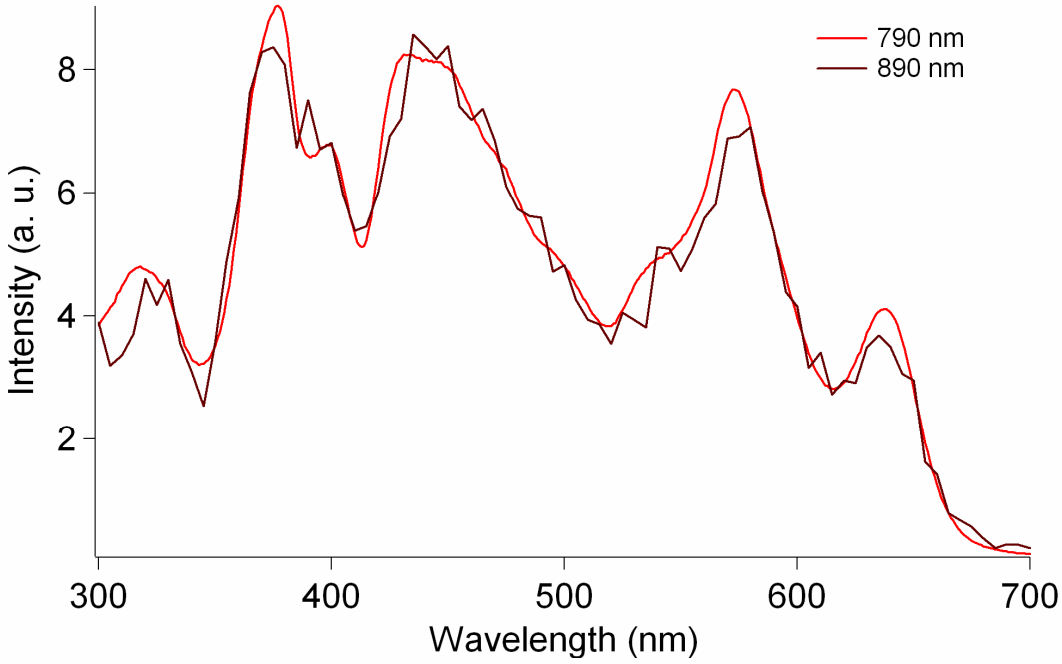
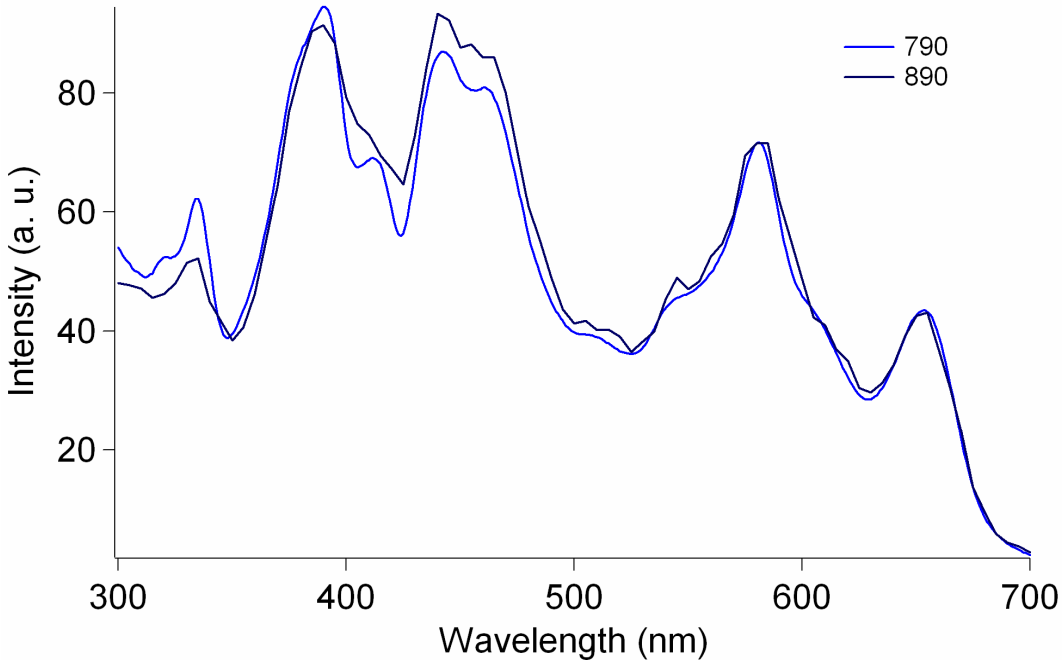


Figure S3. UV-vis absorption spectra of (top to bottom) **1-Ir(tma)$_2$**, **1b-Ir(tma)$_2$**, and **1-Ir(py)$_2$** at room temperature in a broad range of solvents. The inset is the Soret band used for the calculation of the solvatochromic shifts in the manuscript.


790 nm
890 nm
Intensity (a. u.)
2
4
6
8
300
400
500
600
700
Wavelength (nm)


790
890
Intensity (a. u.)
20
40
60
80
300
400
500
600
700
Wavelength (nm)

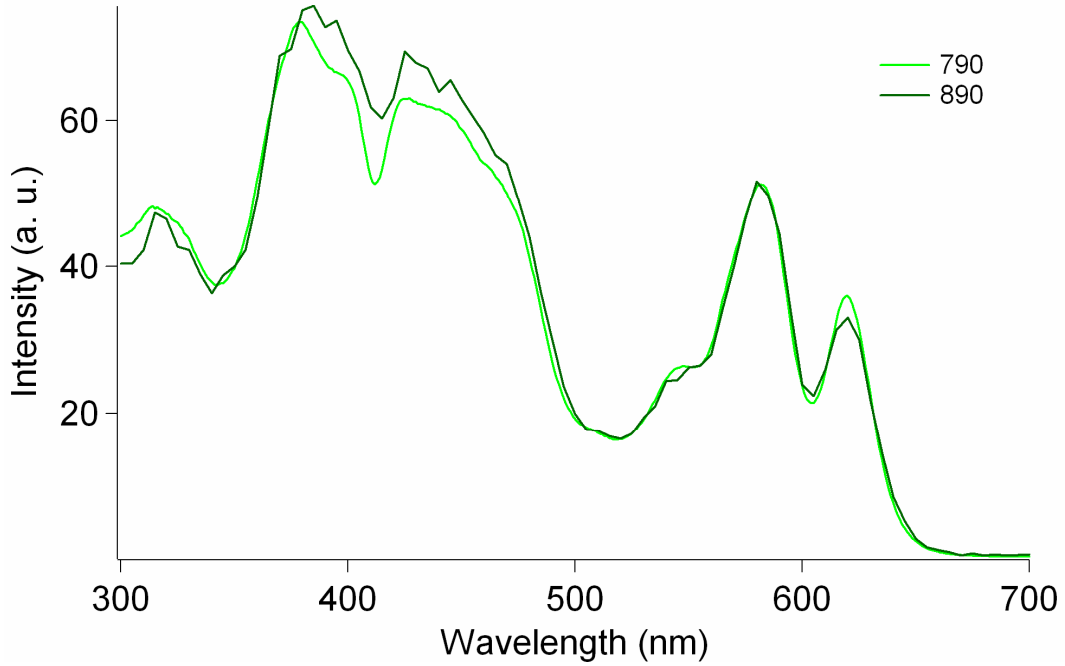


Figure S4. Normalized excitation profiles of (top to bottom): **1-Ir(tma)$_2$**, **1b-Ir(tma)$_2$**, and **1-Ir(py)$_2$** monitored at emission wavelengths of 790 and 890 nm. These profiles support that the two-peak structure we observe in the emission spectra is due to vibrational splitting, and is not representative of emission from two separate states.

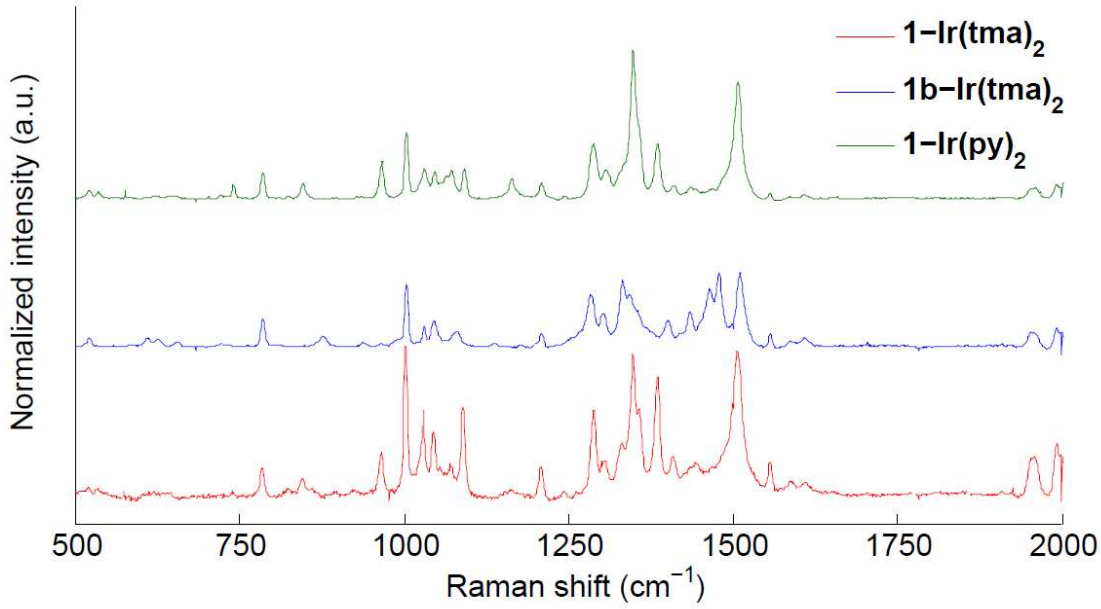


Figure S5. Raman spectra of **1-Ir(tma)$_2$**, **1b-Ir(tma)$_2$**, and **1-Ir(py)$_2$**. Sample excitation into the Soret was achieved with the 488 nm line of an argon ion laser.